BIOCORROSION NETWORK
A SUM-UP OF FIELD EXPERIENCES
TASK 2 CORROSION

- Avesta Sheffield AB, Sweden
- BASF, Germany
- British Steel plc, Swindon Technology centre, UK
- Denmark’s Technical University, DTU, Denmark
- EDF, France
- Instituto per la Corrosione Marina, Italy
- Sintef, Norway
- Swedish Corrosion Institute, Sweden
- University of Portsmouth, UK
Introduction

- Carbon Steel in anaerobic environments, field studies
- Low alloy steel and carbon steel in anaerobic environments, laboratory studies
- Stainless steels anaerobic environments, field and laboratory studies
- Stainless steels in aerobic environments, field and laboratory studies
- Titanium, Nickel and 70Ni30Cu alloy
Carbon steel - Low water corrosion

- A statistical comparison between Normal Low Water Corrosion NLWC sites and Accelerated Low Water corrosion (ALWC) sites
- 22 sites in 39 visits where 10 were ALWC sites.
Accelerated or Normal Low Water corrosion sites

- ALWC site
  - Corrosion rates ~ 0.3 mm/y
  - Local corrosion
  - Corrosion products with poor adherence

- NLWC site
  - Corrosion rates ~ 0.1 mm/y
  - No local corrosion
  - Adherent corrosion products
Statistical method used

- Site ALCW is similar to NLWC
- Site ALCW is not similar to NLWC

ALWC<NLWC  ALWC>NLWC
Parameter comparison

- General environmental influences: Sunlight rates, mean water/air temperatures and geographical orientations: NLWC = ALWC
- The presence of high number of bacteria (SRB/SOB) did not correlate with low-water corrosion problems.
- No difference in the spatial distribution of bacteria in the layer close to steel surface between the sites.
- Sulphides were qualitatively detected on all sites.
Corrosion products
The number of culturable bacteria were everywhere lower in the innermost layer in contact with the steel.

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>ALWC</th>
<th>NLWC</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORGANIC MATTER</td>
<td>HIGHER</td>
<td>LOWER</td>
</tr>
<tr>
<td>ALGAE</td>
<td>HIGHER</td>
<td>LOWER</td>
</tr>
<tr>
<td>CHLORIDE</td>
<td>HIGHER</td>
<td>LOWER</td>
</tr>
<tr>
<td>HEAVY METALS</td>
<td>LOWER</td>
<td>HIGHER</td>
</tr>
<tr>
<td>PH</td>
<td>LOWER</td>
<td>HIGHER</td>
</tr>
<tr>
<td>PHOSPHORUS</td>
<td>LOWER</td>
<td>HIGHER</td>
</tr>
</tbody>
</table>
### Statistical significant parameters related to ALWC

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ALWC</th>
<th>NLWC</th>
<th>One tailed t-test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Tidal Range (m)</td>
<td>$3.0 \pm 2.1$</td>
<td>$4.9 \pm 3.0$</td>
<td>ALWC &lt; NLWC P=0.047</td>
</tr>
<tr>
<td>- Data from Baltic Sea excluded</td>
<td>$3.5 \pm 2.1$</td>
<td>$5.3 \pm 2.9$</td>
<td>ALWC &lt; NLWC P=0.075</td>
</tr>
<tr>
<td>Thickness of Corrosion Products (mm)</td>
<td>$9.7 \pm 6.4$</td>
<td>$6.1 \pm 2.8$</td>
<td>ALWC &lt; NLWC P=0.016</td>
</tr>
<tr>
<td>pH undernaeath Corrosion Products</td>
<td>$6.2 \pm 0.7$</td>
<td>$6.8 \pm 0.7$</td>
<td>ALWC &lt; NLWC P=0.021</td>
</tr>
<tr>
<td>Redox Potential of Seawater (mV vs. Ag/AgCl)</td>
<td>$0 \pm 106$</td>
<td>$54 \pm 74$</td>
<td>ALWC &lt; NLWC P=0.05</td>
</tr>
<tr>
<td>Presence of Invertebrates</td>
<td>75%</td>
<td>93%</td>
<td>ALWC &lt; NLWC P=0.07</td>
</tr>
<tr>
<td>Presence of Algae</td>
<td>90%</td>
<td>67%</td>
<td>ALWC &lt; NLWC P=0.06</td>
</tr>
<tr>
<td>Organic Carbon (%)</td>
<td>$2.2 \pm 0.5$</td>
<td>$1.4 \pm 0.5$</td>
<td>ALWC &lt; NLWC P=0.028</td>
</tr>
<tr>
<td>Organic Hydrogen (%)</td>
<td>$1.2 \pm 0.2$</td>
<td>$0.8 \pm 0.2$</td>
<td>ALWC &lt; NLWC P=0.041</td>
</tr>
<tr>
<td>Organic Nitrogen (%)</td>
<td>$0.36 \pm 0.06$</td>
<td>$0.31 \pm 0.02$</td>
<td>ALWC &lt; NLWC P=0.06</td>
</tr>
<tr>
<td>TOC of Seawater (mg l$^{-1}$ O$_2$)</td>
<td>$14.6 \pm 13.5$</td>
<td>$7.2 \pm 7.9$</td>
<td>ALWC &lt; NLWC P=0.036</td>
</tr>
<tr>
<td>MPN$_{SOB}$ (Cells g$^{-1}$ CP dry weight)</td>
<td>$6.5 \times 10^5 \pm 2.1 \times 10^6$</td>
<td>$3.5 \times 10^3 \pm 5.9 \times 10^3$</td>
<td>ALWC &lt; NLWC P=0.08</td>
</tr>
</tbody>
</table>
Carbon steel - anaerobic clay, bog - corrosion rates

- Measurements with a probe
- EIS - Electrochemical Impedance Spectroscopy
- Linear Polarisation Resistance measurements
<table>
<thead>
<tr>
<th>Site, Denmark</th>
<th>Depth in clay</th>
<th>Exposure time</th>
<th>Rate EIS, μm/y</th>
<th>Weight loss, μm/y</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vallensbæk, autumn, 2-12°C autumn</td>
<td>30 cm</td>
<td>6 months</td>
<td>200-400</td>
<td>10</td>
<td>bank, stream Cl- 240ppm</td>
</tr>
<tr>
<td>Utterslev, 5-15°C, spring</td>
<td>30 cm</td>
<td>6.5 months</td>
<td>5-10</td>
<td>30</td>
<td>bank, stream</td>
</tr>
<tr>
<td>Arresø bog, late autumn</td>
<td>30 cm</td>
<td>47 days</td>
<td>init: 200 end: 10</td>
<td>5</td>
<td>marin sediment, stagnant</td>
</tr>
<tr>
<td>Kyndby, summer, 15 °C</td>
<td>70 cm</td>
<td>15 days</td>
<td>init: 145</td>
<td>20</td>
<td>SRB active mud, stagnant</td>
</tr>
</tbody>
</table>
Estimation of corrosion rates with EIS

- The equivalent circuit was not valid for all measurements, but this approach was taken to examine the general change in parameters.
- The risk of erroneous corrosion rate estimation was large especially if porosity was combined with a reactive film.
Field tests in Denmark

- Corrosion rate could not be correctly assessed by EIS if sulphide was present.
- DC-polarisation scans were very much effected by hysteresis and did not give a reliable corrosion rate.
- Galvanostatic pulse measurements did not give reliable results.
Cont. Field tests in Denmark

- Weight loss measurement was the most reliable technique, but it only gave accumulated corrosion rate.
- All techniques were sensible to the fact that the soil is heterogeneous and that the positioning of probe or weight loss coupons is critical.
- The most active SRB-environment Kyndby was at short time exposure not the most corrosive.
Low alloy steel and carbon steel - laboratory tests

### Material

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%Cr</td>
<td>0.066</td>
<td>0.27</td>
<td>0.95</td>
<td>0.005</td>
<td>0.005</td>
<td>1.02</td>
<td>&lt;0.005</td>
<td>0.04</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>2%Cr</td>
<td>0.081</td>
<td>0.24</td>
<td>0.93</td>
<td>0.006</td>
<td>0.005</td>
<td>1.96</td>
<td>0.006</td>
<td>0.06</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>0.5%Mo</td>
<td>0.069</td>
<td>0.25</td>
<td>0.91</td>
<td>0.006</td>
<td>0.004</td>
<td>0.02</td>
<td>0.490</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>0.5%Cu</td>
<td>0.066</td>
<td>0.25</td>
<td>0.97</td>
<td>0.006</td>
<td>0.004</td>
<td>0.03</td>
<td>&lt;0.005</td>
<td>0.04</td>
<td>0.51</td>
</tr>
<tr>
<td>1.85%Si 0.25Cr</td>
<td>0.060</td>
<td>1.85</td>
<td>1.04</td>
<td>0.014</td>
<td>0.004</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.35%Si 0.55%Cr</td>
<td>0.080</td>
<td>1.35</td>
<td>1.00</td>
<td>0.015</td>
<td>0.005</td>
<td>0.56</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CrNiCu</td>
<td>0.057</td>
<td>0.43</td>
<td>0.74</td>
<td>0.012</td>
<td>0.005</td>
<td>0.90</td>
<td>-</td>
<td>0.23</td>
<td>0.29</td>
</tr>
<tr>
<td>Mild steel</td>
<td>0.110</td>
<td>0.04</td>
<td>0.53</td>
<td>0.012</td>
<td>0.007</td>
<td>0.02</td>
<td>-</td>
<td>0.02</td>
<td>&lt;0.02</td>
</tr>
</tbody>
</table>
Experimental

- Dual cell arrangement
  - Filtered 0.2 µm Porthsmuth seawater
  - consortia COT, SOB, SRB to one of the cell
## Results - low alloy steel and carbon steel, laboratory test

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Corrosion rate (mm/y)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Cr</td>
<td>1.44</td>
<td>Inoculated</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>Uninoculated</td>
</tr>
<tr>
<td>2% Cr</td>
<td>1.38</td>
<td>Inoculated</td>
</tr>
<tr>
<td></td>
<td>0.39</td>
<td>Uninoculated, black deposits</td>
</tr>
<tr>
<td>0.5% Mo</td>
<td>1.59</td>
<td>Inoculated</td>
</tr>
<tr>
<td></td>
<td>0.13</td>
<td>Uninoculated</td>
</tr>
<tr>
<td>0.5% Cu</td>
<td>1.06</td>
<td>Inoculated</td>
</tr>
<tr>
<td></td>
<td>0.13</td>
<td>Uninoculated</td>
</tr>
<tr>
<td>1.8%Si, 0.25% Cr</td>
<td>1.40 (2.28)</td>
<td>Inoculated</td>
</tr>
<tr>
<td></td>
<td>0.17 (0.16)</td>
<td>Uninoculated</td>
</tr>
<tr>
<td>CrCuNi</td>
<td>0.50 (1.02)</td>
<td>Inoculated</td>
</tr>
<tr>
<td></td>
<td>0.13 (0.16)</td>
<td>Uninoculated</td>
</tr>
<tr>
<td>Mild steel</td>
<td>1.64</td>
<td>Inoculated</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>Uninoculated</td>
</tr>
</tbody>
</table>
Low alloy steel cont.

- Inoculated cell
  - Black deposits, increased corrosion rates
- Uninoculated cell
  - Low corrosion rates
Biological drum reactor - laboratory tests

- Carbon steel AISI-SAE 1008
  - Three experiments, duration time: 70-120 days
  - 40 coupons, Ø10 mm in a 120 dm³ drum reactor containing artificial seawater (ASTM D1141-80) inoculated with SRB
  - Anaerob environment by Nitrogen gas purging
  - Inoculation with crude oil terminal SRB
  - Flow by rotation: 60 rpm
  - Temperature: 20-22°C
  - Chloride content: 17.7 ppm
Biological drum reactor, results

- General corrosion with a tendency to locality
- Initial corrosion rates determined with LPR and DC: 10 µm/y that increased to 2 mm/y after film formations
- Corrosion rates determined with EIS:
  - initial 10-100 µm/y
  - final 1-2.5 mm/y
- EIS: large capacitance as sulphide concentration increased
- OCP: -750 mV/SCE that increased after film formation to -650 mV/SCE
Stainless steels

- Anaerob environment
  - Seawater, clay
  - Wastewater treatment
- Aerob environment
  - Seawater
  - River water
  - Wastewater
Crevice corrosion resistance in anaerobic seawater

- Material: Stainless steel grades, 1.4404 (316L), 1.4539 (904L), 1.4462 (2205), 1.4547 (254SMO) and 1.4652 (654SMO) with crevice formers of polyethylene

- Environment: Marine anaerobic bacteria SRB from a natural source fed with milk
  - Temperature: 30°C, pH 6.85-7.1
  - Sulphide: 320-500 ppm
Stainless steels and anaerobic environment - seawater

- Electrochemical measurements: OCP, potentiodynamic polarisation scans (cathodic, anodic)
- Simulation of ennoblement in anaerobic environment corresponding to a coupled situation between anaerobic environment and aerobic environment (2mv/15 min)
Stainless steels - anaerobic seawater, crevice corrosion

- OCP in anaerobic environment \( \sim -550 \text{ mV/SCE} \)
- No corrosion in a pure anaerobic environment
- Coupled situation in positive or negative direction can give an increased risk for crevice corrosion

Risk for crevice corrosion
Except 654SMO
No Corrosion
Corrosion
Stainless Steel - Seawater polluted with sulphide

- 1.4401(316), 1.4462 (2205), 1.4447 (254SMO), 1.4652 (654SMO)
- Crevice samples simulating real flange situations.
- Exposure in a tank (5m³) with recirculated seawater (30-40 dm³/h) for 95 days.
- Addition of 1000 ppm Na₂S in the start of the test.
Results - SS in Seawater polluted with sulphide

- OCP ~ -515 mV/SCE,
- Redox ~ -500 mV/SCE
- Attacks on 1.4401 (316) at welds and at dark brown spots in the fusion line
- Pitting on 1.4401 (316) above the waterline
Chlorinated seawater

- 1.4401(316), 1.4462 (2205), 1.4447 (254SMO), 1.4652 (654SMO) and nickel based alloys N06625, N10276
- Crevices simulating real flange situations
- Residual chlorine 7.7-13 ppm (~10 ppm)
- pH 8.0-8.1, Temperature 45°C
- No slime or biofouling after 95 days exposure
- Corrosion on all samples except 654SMO
Anaerobic clay environment in seawater at Genova harbour

- Stainless steel grades
  - 1.4013(430)
  - 1.4301(304)
  - 1.4401(316)

- Exposure 6 months

- pH 7.6

- Sulphur content 2.65-3.15 mol/dm³

- OCP: 304, 316 ~ -500

- OCP: 430 ~ -500 to -600
Stainless steels in aerobic environment

- Seawater - MAST program - Biofilm project, Marine Biofilms on stainless steels, Effects, monitoring and prevention
- Fresh water and industrial system
  - River Rhine
  - Chemical plants
  - Wastewater
  - Nuclear Power Plants
MAST II

- Exposure in coastal seawaters in Europe with and without crevices (POM)
- Biofilm samples were collected to relate electrochemical effects to biofilm components

Table 1. Stainless steel grades exposed in the MAST II Program.

<table>
<thead>
<tr>
<th>EN</th>
<th>Trade name</th>
<th>Chemical composition, (% weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>1.4435</td>
<td>316L</td>
<td>17.2</td>
</tr>
<tr>
<td>1.4462</td>
<td>2205</td>
<td>22</td>
</tr>
<tr>
<td>1.4460</td>
<td>UR47N</td>
<td>24.7</td>
</tr>
<tr>
<td>1.4507</td>
<td>UR52N+</td>
<td>25</td>
</tr>
<tr>
<td>1.4410</td>
<td>SAF 2507</td>
<td>24.9</td>
</tr>
<tr>
<td>1.4547</td>
<td>254SMO</td>
<td>19.9</td>
</tr>
<tr>
<td>1.4652</td>
<td>654SMO</td>
<td>24.5</td>
</tr>
<tr>
<td>1.4563</td>
<td>SAN28</td>
<td>26.7</td>
</tr>
<tr>
<td>1.4537</td>
<td>URSB8</td>
<td>24.9</td>
</tr>
<tr>
<td>1.4529</td>
<td>URB26</td>
<td>20</td>
</tr>
</tbody>
</table>
Geographical locations

- Exposure time: summer 93 - spring 94
Seawater exposure

- Potential ennoblement and final value at all stations and seasons similar
- Initial OCP varied
- Incubation time varied with season
Seawater exposure, cont.

- No correlations with ennoblement:
  - pH
  - geographic location
  - stainless steel compositions
  - chlorophyll a
  - salinity
  - ash
  - organic matter contents, biomass

- Related to ennoblement:
  - Temperature
    - 20°C rapid increase of potential
    - 30°C rapid increase of potential
    - 40°C no ennoblement
  - EPS content (satisfactory correlation)
Biofilm growth and cathodic current evolution - SVET

- After one day of exposure, the oxygen reduction current was uniformly distributed over the whole stainless steel surface (1.4410, SAF2507)
- 50 days exposure in Baltic seawater in the laboratory showed preferential sites for a fast oxygen reduction
- By adding an enzymatic inhibitor the active sites were deactivated
Corrosion after exposure

- Crevice corrosion was found on 316 L exposed in Genoa, Italy and Trondheim, Norway
- The more alloyed steel grades either austenitic or duplex grades appeared to be resistant to crevice corrosion after 250 days (6000 hours) at all stations
- Depassivation (discolouration) appeared but there was no weight loss
MAST II - Experiences on real industrial components

- Cases of corrosion failures that occurred in seawater systems at installations in the North Sea
  - Crevice corrosion in flanges
  - Treads with critical geometry for initiation
  - Improper surface treatment
  - Chlorinated systems on higher alloyed 6Mo Stainless Steel
Industrial systems

- Chemical plant using cooling water from River Rhine, 1.4401
  - Flow 1.5-2 m/s
  - Cl⁻ ~ 50-200 ppm,
  - Temperature 30-35°C
  - Pitting corrosion - pinhole leaks on welds
  - No corrosion on base material
  - Unpickled welds remaining heat tints

- Tubular heat exchanger
  - leaked after 5 years service 1.4462(2205) welded with (X2CrNiMoN17-13-5)
  - Temperature 30-50°C
  - Used for some weeks/year - often stagnant flow conditions dominated
  - River water remained in the tubes
Wastewater treatment

- Corrosion of SS 1.4404 (316L) pipes in a wastewater treatment plant after modernising with biological nitrification/denitrification unit; pharmaceutical plant
- 19 year corrosion free
- Six months after taking new unit into use:
  - Pitting at welded joints
  - Pitting nearly on nearly all circular welds
  - Pitting on base material but no leaks
  - Pitting and crevice corrosion on flanges and nozzles
Wastewater treatment, cont.

- Field tests in the final stages in four plants in Sweden for one year on 1.4301 (304), 1.4401 (316), 1.4462 (2205)
- Ennoblement: in two plants and with values close to the same as in seawater in one of the plants
- Corrosion was found on 1.4401 (316) in one plant both on welds and base material
- Corrosion on 1.4301 (304) in three of the plants
- No corrosion on 1.4461 (2205)
Nuclear Power plant

- Fire protection system in a power plant and waste treatment system
- 1.4301 (304) 18-10 welded tubes
- 300-500 ppm chloride
- 100 ppm sulphate, pH 7.5-7.9
- Room temperature
-Leaks on the welds after one year

- Loop test with river water and sterilised water
- Enhanced corrosion in raw water loop
- Biofilm development on unpickled welds
Titanium, Nickel and 70Ni70Cu alloy - laboratory study

- Immersion in a tank of 100 dm³ of natural seawater changed with renewal 100dm³/h and in unchanged sterilised seawater, temperature: 25°C

- Ti: increase in the free corrosion potentials ~250mV/SCE in natural water

- Ni: Similar free corrosion potentials in natural and steril water but corrosion was found by weight loss

- 30Ni70Cu alloy: Similar free corrosion potentials in both environment but corrosion was found by weight loss
Conclusions

Discussion